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SOLDER COMPOSITION

BACKGROUND

Generally speaking, solder is a material used to provide connections either between various items or to secure an item to a substrate. Solder is used in several technical fields, such as electrical, mechanical, or thermal; however, the specific composition of solder or type of solder alloy varies widely between technical fields and even within a given field, depending on the application. Traditionally, solder largely consisted of lead as a result of its physical and chemical characteristics (i.e., wettability, melting point, rate of thermal expansion, etc.); however, lead solder became known as a source of environmental pollution and federal legislation mandated a reduction in the content of lead in solder.

As a result, lead-free solder was introduced into various technical fields and is currently used for numerous applications without issue. As disclosed in U.S. patent numbers 5,066,544; 5,918,795; and 6,371,361, lead-free solder or reduced lead content solder is successfully applied to soldering electronic components in both the microelectronic and conventional electronic fields.

However, there exist other technical fields where the aforementioned lead free solders are deficient. Within the technical field of soldering onto a substrate, such as an automobile window or windshield, known lead-free solders are less desirable because they contain alloy compositions which possess a coefficient of thermal expansion nearly twice that of a glass substrate. As a result, the solder can separate from and/or crack the

glass substrate during a substantial change in climatic temperature. This situation is known as thermal shock.

U.S. Patent number 6,319,461, issued to Domi *et al.* discloses a lead free solder for soldering to a ceramic or glass substrate to resist thermal shock. The Domi *et al.* invention includes titanium as its essential component in combating thermal shock; however, the price and properties of titanium when included in a solder give rise to concerns over cost and workability of the solder at certain temperatures. As a result, the titanium laden Domi *et al.* solder composition is restricted to a liquids temperature not greater than 400°C.

A need exists in the art for a cost-effective, workable, lead-free solder composition suitable for use on a glass substrate having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

SUMMARY

The present invention has been developed to overcome many limitations and disadvantages of known lead-free solders, and to generally fulfill a need in the art for a lead-free solder composition having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

The present invention provides a lead-free solder composition for soldering to a glass substrate, wherein the solder composition includes tin (Sn) and silver (Ag) as well as a granular additive material having a low coefficient of thermal expansion to combat thermal shock and the percent weight of the solder and granular additive are at least 97% and at least 3%, respectively.

The solder composition of the present invention can further include bismuth (Bi) wherein the percent weight of the solder, including bismuth, is between 61% and 39% tin (Sn), between 1% - 3% silver (Ag) and between 59% and 37% bismuth (Bi).

The granular additive of the present invention can be fused silica (SiO_2) or Invar®, encapsulated in a lead-free, wettable, metal alloy such as copper (Cu), nickel

(Ni) or silver (Ag). The granular additive may also be 36% $\pm$ 1% weight nickel (Ni) alloy or 64% $\pm$ 1% weight iron (Fe) alloy.

It is an object of the present invention to provide a lead-free solder composition which is cost effective, easy to manufacture, and easy to apply to a substrate.

It is another object of the present invention to provide a lead-free solder composition whose percent weight between solder and granular additive can be adjusted to coincide with the coefficient of thermal expansion of the substrate to which the solder is to be secured.

It is still another object of the present invention to be capable of use in connection with a layer of indium to promote greater adhesion to a substrate.

The present invention also includes a solder composition including a mixture of elements having tin (Sn) and silver (Ag). A granular additive is also included which can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by weight.

In particular embodiments, the granular additive can be pretreated with flux. The flux can include zinc chloride, ammonium chloride and hydrochloric acid. The mixture of elements can include by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag). The mixture of elements can further include bismuth, in which the mixture of elements can include by weight about 61% - 39% tin (Sn), about 59% - 37% bismuth (Bi) and about 1% - 3% silver (Ag).

In some embodiments, the granular additive can be about 30% of the solder composition by weight. In one such solder composition, the mixture of elements can include by weight about 95% tin (Sn) and about 5% silver (Ag). In another such solder composition, the mixture of elements can include by weight about 75% tin (Sn) , about 23% bismuth (Bi) and about 2% silver (Ag).

In other embodiments, the granular additive can be about 20% of the solder composition by weight. In one such embodiment, the mixture of elements can include by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag). In

another such embodiment, the mixture of elements can include by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag). In yet another such embodiment, the mixture of elements can include by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag). In still another such embodiment, the mixture of elements can include by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag). In a further such embodiment, the mixture of elements can include by weight about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag).

The present invention also includes a solder composition including a mixture of elements including tin and silver. A granular additive is also included and includes a material having a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

In particular embodiments, the granular additive can include iron, and can also include iron and nickel. In addition, the granular additive can be pretreated with flux which can include zinc chloride, ammonium chloride and hydrochloric acid.

The present invention also includes a method of forming a solder composition. A molten mixture of elements having tin and silver is formed. A granular additive is added to the molten mixture of elements. The granular additive can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by weight.

In particular embodiments, the granular additive can be pretreated with flux before adding the granular additive to the molten mixture of elements.

The present invention also includes a method of forming a solder composition including forming a molten mixture of elements having tin and silver. A granular additive is added to the molten mixture of elements. The granular additive includes a material with a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of particular embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. 1 is an assembly of a solder composition on a hardware component in accordance with an embodiment of the invention before melt.

FIG. 2 is an assembly of the solder composition secured to a hardware component and a substrate in accordance with an embodiment of the invention and including an enhanced bonding sub layer of Indium after melt.

DETAILED DESCRIPTION

Referring to FIGs. 1 and 2, an embodiment of a solder composition is shown generally at 10 on a hardware component 20, such as a copper terminal, and a substrate 30. The solder composition 10 includes solder 12 and a granular additive 14 having a low coefficient of thermal expansion. The solder 12 includes tin and silver with a percent composition by weight of 95-97% tin (Sn) and between 5-3% silver (Ag). Additionally, the solder 12 may also include bismuth (Bi), wherein said percent composition by weight of the three components is 61-39% tin (Sn), 1-3% silver (Ag) and 59-37% bismuth (Bi).

As an alternative embodiment, for securing the solder to a glass substrate, the glass substrate may be coated with a layer of indium 46, approximately 50 microns thick, to improve bonding the hardware 20 to the substrate 30.

Further referring to FIGs. 1-2, the granular additive 14 with a low coefficient of thermal expansion is added to the solder 12. The granular additive 14 may be any wettable material having a low coefficient of thermal expansion such as fused silica, zirconium oxide, Invar®, or an alloy of 36% weight nickel (Ni) or 64% weight iron (Fe).

To improve wettability of the fused silica, it may be encapsulated in a metal such as copper, nickel, or silver. The size of the granular material 14 may range from 5 to 400 microns; however, particles ranging from 10 to 250 microns are preferred.

The percent weight of the solder 12 and granular material 14 for the solder composition 10 can be contingent upon the coefficient of thermal expansion of the substrate 30. By way of example, when using fused silica as the granular material 14, the percent weight of the solder composition 10 is at least 97% solder 12 and at least 3% granular material 14 to secure the solder composition 10 (and included hardware 20) to a glass substrate 30 having a coefficient of thermal expansion of 85×10^{-7}.

Referring specifically to FIG. 2, the solder composition 10 is placed on the hardware 20 and secured to the substrate 30 by conventional means, i.e., applying heat to melt the solder 12 and attach the hardware 20 to the substrate 30, thereby trapping the granular material 14 between the hardware 20 and the substrate 30. When the joined hardware 20 and substrate 30 are exposed to low climatic temperatures, the solder 12 can attempt to contract at a rate higher than that of the substrate 30; however, the trapped granular material 14 will prevent the high contraction rate of the solder 12 and adsorb the stress created by same, causing the substrate 30 to receive little or no stress from the contraction, thereby preventing thermal shock. If a layer of indium 46 (FIG. 1) is employed, a region 46a having a mixture of solder 12 and indium can be formed when melted.

In one embodiment, when preparing a solder composition 10 including granular Invar® as the granular additive 14, the mixture of elements of solder 12 can be first brought into a molten state. Flux is added to the granular Invar® and then the Invar® is mixed into the solder 12 to form the solder composition 10. The Invar®/flux mixture can be added to the solder 12 while wet or can be predried to reduce splattering. The flux pre-treats the Invar® and allows the Invar® to easily wet with the solder 12. The flux can be in liquid form and can contain for example, zinc chloride, ammonium chloride, and hydrochloric acid. When flux is used, encapsulation of the Invar®

granules by another metal is not necessary. Once mixed, the solder composition 10 can then be formed or cast into desired shapes.

The Invar® granules are typically spheres of an alloy that has about 36% nickel (Ni) by weight and about 64% iron (Fe) by weight. In one embodiment, the Invar® can have a particle size ranging from 50-140 microns. If desired, the Invar® with such a size can be sifted to remove particles below 100 microns so that particles having a size between about 100-140 microns can be added to the solder 12. The Invar® can in some embodiments be 20% - 30% of the solder composition 10 by weight, with the mixture of the elements of the solder 12 being the remaining 70% - 80% of the solder composition 10 by weight.

In addition to the composition ranges previously described for the solder composition 10, the Applicants have found particular solder compositions 10 that are suitable for soldering to glass. For example, in one solder composition 10, the solder 12 can be about 95% tin (Sn) and about 5% silver (Ag) by weight. In this solder composition 10, the 95Sn 5Ag solder 12 makes up about 70% of the weight of the solder composition 10 and the added Invar® makes up about 30%.

In another solder composition 10, the solder 12 can be about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 75Sn 23Bi 2Ag solder 12 makes up about 70% of the weight of the resulting solder composition 10 and the Invar® makes up about 30%.

In yet another solder composition 10, the solder 12 can be about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 62Sn 36Bi 2Ag solder 12 makes about 80% of the weight of the solder composition 10 and the added Invar® makes up about 20%.

In still another solder composition 10, the solder 12 can be about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 72Sn 26Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

In a further solder composition 10, the solder 12 can be about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 78Sn 20Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

In yet a further solder composition 10, the solder 12 can be about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 83Sn 15Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

In still a further solder composition 10, the solder 12 can be about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 88Sn 10Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

While this invention has been particularly shown and described with references to particular embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims. For example, although the solder composition 10 is suitable for use on glass, solder composition 10 can be used on other substrates and in other fields. In addition, although the solder composition 10 has been described as being melted by applying heat, in some embodiments, the solder composition 10 can be used for spin soldering where friction generated by a spinning electrical terminal against a substrate heats and melts the solder composition 10 therebetween.